CANEUS

# High Sensitivity, Low Power Nano Sensors and Devices for Chemical Sensing

Jing Li[1], Dan Powell[2], Stephanie Getty[2], Yijiang Lu[3]

[1]NASA Ames Research Center

[2]NASA Goddard Space Flight Center

[3]Eloret Corporation, NASA Ames Research Center, Moffett Field, CA

Coordinated by: Dan Powell,

Goddard Space Flight Center, Greenbelt, MD

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# *Abstract*

The chemical sensor market has been projected to grow to better than $40 billion dollars worldwide within the next 10 years. Some of the primary motivations to develop nanostructured chemical sensors are monitoring and control of environmental pollution; improved diagnostics for point of care medical applications; reductions in measurement time, sensor size, and power consumption; improvement in measurement precision and accuracy; and improved detection limits for Homeland security, battlefield environments, and process and quality control of industrial applications. In each of these applications, there is demand for sensitivity, selectivity and stability of environmental and biohazard detection and capture beyond what is currently commercially available. It is believed that the emerging field of nanotechnology can play an important role in realizing these goals, and the following concept development represents a significant step in that direction.

Nanotechnology offers the ability to work at the molecular level, atom by atom, to create large structures with fundamentally new molecular organization. It is essentially concerned with materials, devices, and systems whose structures and components exhibit novel and significantly improved physical, chemical and biological properties, phenomena, and process control due to their nanoscale size.

One such nanotechnology-enabled chemical sensor has been developed at NASA Ames leveraging nanostructures, such as single walled carbon nanotubes (SWNTs) and metal oxide nanobelts or nanowires, as a sensing medium bridging a pair of interdigitated electrodes (IDE) realized through a silicon-based microfabrication and micromachining technique. The IDE fingers are fabricated on a silicon substrate using standard photolithography and thin film metallization techniques. It is noteworthy that the fabrication techniques employed are not confined to the silicon substrate. Through spin casting and careful substrate selection (i.e. clothing, glass, polymer, etc.), additional degrees of freedom can be exploited to enhance sensitivity or to conform to unique applications. Both in-situ growth of nanostructured materials and casting of nanostructured dispersions were used to produce analogous chemical sensing devices.

Sensors developed have been exposed to nitrogen dioxide, acetone, benzene, nitrotoluene, chlorine, and ammonia and repeatedly sensed these analytes in the ppm to ppb concentration range at room temperature. In addition, development of metal oxide nanobelt based sensors have been explored to facilitate significantly lower temperature operation (~150°C) than that of conventional metal oxides sensors (~500°C) with similar sensing performance.

Due to their large surface area, low surface energy barrier and high thermal and mechanical stability, nanostructured chemical sensors offer higher sensitivity, lower power consumption and a more robust solution than most state-of-the-art systems making them attractive for defense and space applications, as well as a variety of other commercial applications such as monitoring hazardous incoming raw materials and detecting toxins which may evolve from industrial processes. Leveraging micromachining technology, light weight and compact sensors can be fabricated, in wafer scale, with high yield and at low cost. Additionally, the wireless potential of such sensors can be leveraged to network mobile and fixed-base detection and warning systems for civilian population centers, military bases and battlefields, as well as other high-value or high-risk assets and areas.

# 1. Rationale for Recommendation

Chemical sensors have a wide application spectrum from space exploration to homeland security and commercial applications, and the chemical sensor market is projected to exceed $40 billion US dollars in next 10 years according to Sensors Business Digest 2001.

Here we recommend a cohesive set of micro- and nanotechnologies which yield a viable commercial chemical sensor which exhibits enhanced chemical detection, precision, and accuracy and presents a significantly smaller footprint, lower power-consumption rates, and lower risk of device failure than current state-of-the-art devices. Through application of advanced micro- and nanofabrication techniques, a high density molecular sensing device can be produced to selectively sense many different analytes of interest dispersed at low concentration in complex chemical mixtures. Single sensor developments have been parallelized to yield 32-sensor arrays with a target of producing high density arrays (i.e. $10^3$-$10^6$ sensors per cm$^2$) within 5 years. The initial device-development and basic research for this technology has been funded by NASA and FAA through interagency agreements over the past several years and the first space flight demonstration of these technologies has been facilitated through the Applied Nanotechnology group at NASA's Goddard Space Flight Center.

The development of recommended chemical sensor and nanodevices is in alignment with the future development commitment NASA has embraced. Further, by accepting these technologies for flight demonstration NASA has secured their status as the first applied Nanotechnology in space and enabled the first steps toward practically-sized space systems for future unmanned science and exploration developments and established a benchmark for future enabling technologies development. This year, NASA has invested between $500,000 and $600,000 in the development of these technologies and has realized a 32-channel sensor chip employing several different nanostructured materials, a complete electronic system for sensing signal acquisition, and a pneumatic pathway for periodic sample-gas delivery on orbit. This sensor module that has been developed will be deployed for trace chemical detection demonstration via a Boeing Delta IV launch vehicle secondary payload berth at approximately 500km.

Each sensing channel within the 32-channel array can be tuned to optimal detection of a particular analyte by selecting for application those nanostructured materials best suited to detect individual chemical signatures of interest. Individual analyte detection amplitudes can then be multiplexed to sense a multitude of species simultaneously. Using pattern recognition techniques, our sensor array can digitize the chemical information for real-time display and decision making. This sensor array approach is similar to that previously reported as the 'electronic nose' and the 'electronic tongue'. Using the nanomaterials for making the sensor array and even possible to make high density array, our nano electronic nose and tongue will have better detection capability in terms of high discrimination and identification power for chemical analysis.

Ground-based research shows that the recommended nanosensor technologies provide high sensitivity (ppm-ppb detection levels) and low power consumption ($\mu$W-mW peak load per channel) with high selectivity for selected analytes. This flight system uses a standard RS-422, 9600 baud and 8N1 connector to interface with standard electronic systems. Its uniqueness of compact size, low mass, and ease of integration distinguishes it as a true dual-use technology. Given that much, if not all, of the initial system architecture, developed by NASA, can be directly leveraged for civilian and defense use. Ground-based research also shows that the selectivity of

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detection for different analytes and sampling environments can be further enhanced by optimizing the combination of nanostructures employed.

By employing nanotechnology to work at the atomic and molecular level, we are able to modify the surface and bulk properties of nanostructures with different physiochemical and biological characteristics and to miniaturize the sensor. The resultant high density sensor arrays and orthogonal array design can greatly increase overall detection capability by imparting redundant sensing elements to minimize the noise to enlarge the signal to noise ratio, while offering simultaneous sensing of a variety of analytes via the unique physiochemical and biological properties of each nanostructure employed.

The strategy behind this unique sensing technology which is to develop a universal platform that can be used for different chemicals, and also can be used for different physical states, such as gases, liquids and solids. Modifying the surface and bulk of nanostructures with bio molecules, such as enzyme, antigen, bacteria, through the IDE structure the sensor can detect bio species, such as pathogens, bacteria and other bio hazardous materials in liquid phase. This type of sensor can be used to detect the headspace sample of a solid, such as explosives. We have tested our sensors to nitrotoluene (a stimulant of TNT) with an estimated detection limit of 254ppb. Fabrication process has been developed for large scale production. Figure 1 shows the recommended nanosensor under development at NASA Ames and a sample $NO_2$ sensor response curve.



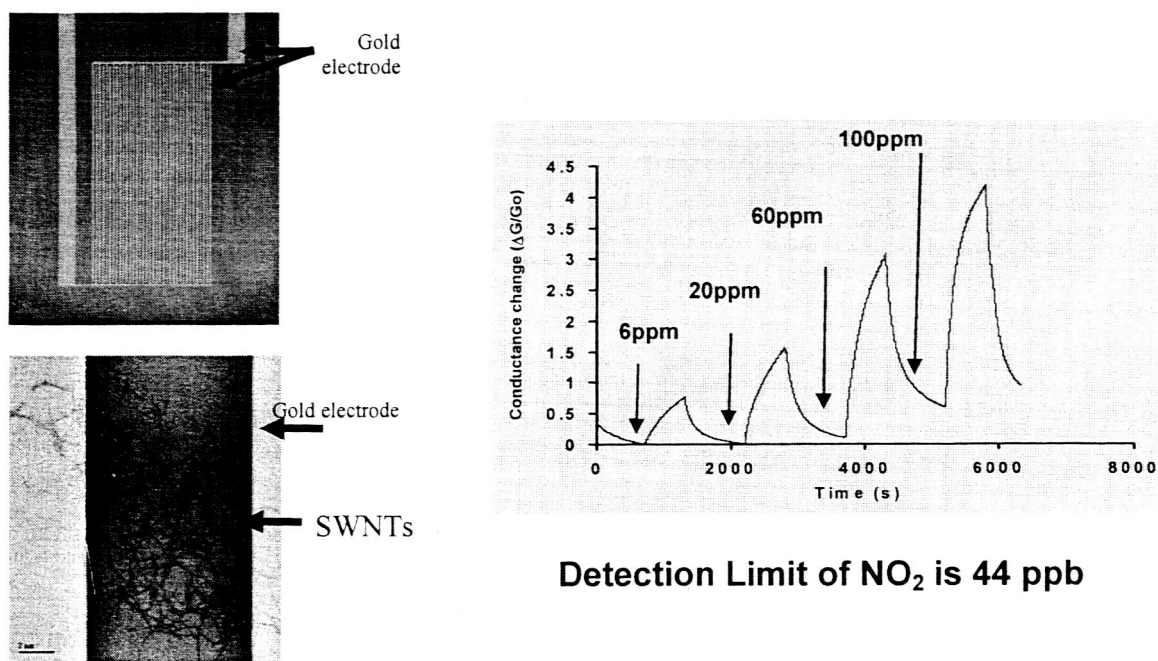**Detection Limit of $NO_2$ is 44 ppb**

*Figure 1: Nanosensor and its response to $NO_2$ at different concentrations. Image of interdigitated electrode (upper left); Carbon nanotubes across gold electrodes (lower left); Sensor response curve to $NO_2$ (right).*

## 2. Current State-of-the-Art

Currently, there are five major types of chemical sensors on the market: 1) electrochemical cells, 2) semiconductor oxides, 3) conducting polymer and polymer composites sensors, 4) surface acoustic wave sensors, 5) catalytic beads. Each of them has advantages and disadvantages as described below:

*Electrochemical cells:* Electrochemical cells work based on the half-cell reaction potential. So, they are very specific for analytes. On the other hand, they are limited to certain analytes that are electrochemically active, such as CO, $H_2S$.

*Semiconducting metal oxides:* Semiconducting metal oxides, such as $SnO_2$ and ZrO have been developed over 50 years and are still under development and improvement. Semiconducting metal oxides are not conductive at low temperature. They work based on the conductivity gain at high temperature (500°C and up) due to the dissociation of oxygen molecules in air and form oxygen anions on the surface. Therefore, the density of holes increases in the bulk of metal oxides matrix to provide measurable conductivity. When hydrocarbons adsorb onto the surface of the oxides, they will be oxidized to form carbon dioxide and water. The conductivity of the metal oxides matrix will change due to the re-dox reaction between the semiconducting oxides and analytes. The big drawback of this sensor is lack of specificity. Any kind of analytes can provide a sensing signal from conductivity change when they are in contact with metal oxides. Also, metal oxides are obviously a power sink, because they have to be operated at high temperature for getting measurable conductivity.

*Conducting polymers and polymer composites sensors:* This type of sensor is based on the organic materials. They are relatively easy to process and most of them are shelf-ready and commercially available materials, especially of those polymer composites. Since they are organic materials, they can only work at low temperature below 120°C in most cases. They belong to non-specific sensor category. They work based on the partition of analytes molecules in two phases, either gas phase or solid/liquid phase. When the gas molecules enter the bulk of solid matrix, the conductivity of conducting polymers and polymer composites will change. The partition coefficient determines the amount of gas molecules equilibrated in the polymer matrix and further change the conductivity. Usually, this type of sensors are not sensitive and especially to those inorganic gases, because these molecules prefer to stay in gas phase.

*Surface acoustic wave sensors (SAW):* SAW sensors use polymers as sensing materials. They measure the frequency change due to the mass loading when gas molecules adsorb onto polymers. It is similar to polymer sensors based on the partition of gas in solid phase. Additional, specific analyte-polymer interaction will has better sensitivity and fast response. However, the electronic circuit for SAW sensor signal acquisition is rather complicated than that of other sensor technologies, because it requires a frequency function generator to perturb the sensor at its resonant vibration mode, and then collect frequency signals before and during the analytes exposure.

*Catalytic beads:* Catalytic bead sensors work based on the combustion of analytes at high temperature. When gases decompose on the catalytic beads, heat will be released or withdrawn; a Whinstone bridge circuit is built for measuring the resistance difference between two arms of the bridge due to the thermal-electrical effect. The sensor response and recovery time of this type sensor is extremely short, almost instantaneously. The drawbacks of this sensor are: 1) very

difficult to detect one chemical specimen; 2) high power consumption rate, because it requires high temperature to burn off analytes.

With the advent of Nanotechnology, much attention has been paid by many scientists to develop nanostructures based chemical sensors and try to overcome the disadvantages of the commercial sensor technologies discussed above. Nanotechnology provides the ability to work at the molecular level, atom by atom, to create structures with fundamentally new molecular organization. As one example of nanostructured materials, carbon nanotubes offer superior performance over conventional approaches due to their remarkable mechanical properties and unique electronic properties as well as the high thermal and structural stability. Nanotechnology based chemical sensors can offer the following:

1. Expand the analytes spectrum much wider than the electrochemical cell can detect from inorganic chemical species in gas and liquid phases to organic vapors and hazardous chemical and biological materials.
2. Operate the chemical sensing at room temperature and overcome the power sink in metal oxides sensors. Also, low temperature operation can avoid combustible hazardous for certain analytes, such as hydrogen, methane and other hydrocarbons.
3. Offer higher sensitivity in detection of ppb concentration level than polymer based sensors and can extend the detectable analytes from organic vapors to inorganic gases and small molecules or chemical and biological species.
4. Design a 2-electrode platform suitable for nano sensing materials for easy and low cost current or voltage measurement to overcome the complicated SAW's electronic system for chemical sensing signal collection. This simple 2-terminal design can be repeated many times for making a sensor array chip to do a complex chemical analysis with pattern recognition techniques.
5. Overcome the huge power consumption of catalytic beads which are currently used in the commercial market. And can also beat the size of catalytic beads (1cm in diameter for single sensor and 0.5cm thick) with a sensor density of > 32 sensors per $cm^2$ and thickness of 0.5mm. The low energy barrier at the surface of carbon nanotubes allows for high-sensitivity room temperature sensing, at very low power consumption rates ($\mu W$ to mW) per sensor. It is thought that these sensors have great potential for embodying a new generation of chemical sensors to detect gas and vapor species. The same sensor platform can be used for detection of chemical species in liquid phase as well as solid phase.

Currently, there are many efforts on the development of nano chemical sensors. Different physiochemical properties of nano materials have been used for chemical sensing with certain sensing platforms. For example, single-walled carbon nanotube (SWNT) based sensors have been demonstrated for the detection of small gas molecules such as $NO_2$ and $NH_3$[1]. A detection level of parts per million (ppm) can be readily reached at room temperature with SWNT sensors in a transistor configuration while it requires a temperature of >350°c for conventional metal-oxide microfilm sensors. The room temperature sensitivity of the SWNT sensors, fabricated like chemical field effect transistors, is attributed to drastic changes in electrical conductivity of semiconducting SWNT induced through charge transfer of gas molecules and Schottky effect at the metal-carbon nanotube junction. However, it is generally difficult to obtain semiconducting SWNTs from as-grown samples, which are typically mixtures of both metallic and semiconducting SWNTs. Even when nanotubes are directly grown on the platform by chemical vapor deposition, there is no control now for the growth of semiconducting or metallic tubes selectively. This often results in fabrication complexity, low

sensor yield and poorly reproducible sensor performance. Recently, a multiple SWNT transistor array coated with a polymer film has been reported [2] to improve sensitivity and selectivity at zero gate voltage. It is not clear if the gating effect itself makes a big contribution to the sensitivity. However, the three terminal transistor configurations make the electronic measurement a complex and a costly platform for chemical sensor applications. Sensors based on carbon nanotube films, in contrast, are less complex and thus less expensive but exhibit poor sensitivity. For example, the resonant-circuit sensors [3, 4] using multi-wall carbon nanotubes (MWNTs) showed sensitivity of only several percent range with a detection limit of 100 ppm for $NH_3$. The low sensitivity of this sensor may be attributed to fewer semiconducting nanotubes in the MWNT film that can be modulated by gas molecules as well as to the poor electric contact between nanotubes and electrodes. A thermoelectric 'nano-nose' fabricated from film of SWNTs bundles [5] also showed a sensitivity of only percent range for gas molecules. The sensitivity of this type of sensor may be affected by the effectiveness of the thermo-electric conversion.

Compared with other nanotechnology based chemical sensors discussed above, our design of the nanostructure-based chemical sensor uses an interdigitated electrode platform, and variety nanostructured materials for chemical sensing.

Here, we describe a simple SWNT sensor platform that combines the advantages of both single nanotube transistors and the film-based nanotube sensors with extended applications to sensitive detection of organic vapors. In this platform, SWNTs form a network or mesh over interdigitated electrodes (IDE) using a solution casting process (see Figure 1) resulting in a large amount of nanotubes to get their statistical properties before and during the analytes exposure to enhance sensor performance in a reproducible manner with longer life. The IDE configuration facilitates effective electric contact between SWNTs and the electrodes over large areas while providing good accessibility for analytes in the form of gas/vapor adsorption or contaminants adsorption/extraction in/from liquid to all SWNTs including semiconducting tubes. This approach offers not only a simplified fabrication process but also a high yield of robust, reliable, and reproducible sensors. This relatively simple fabrication approach is important to keep development and fabrication costs to a minimum and remain competitive in the cost-conscious chemical sensor market. Above all, this type of sensor is amenable to immediately integrate into a variety of sensing system interfaces and platforms.

From our study, it shows that SWNTs are distinct from other nanostructures in that all of the atoms on their surface are exposed to the environment, allowing an overall change in their physiochemical properties. The low energy barrier at the surface of carbon nanotubes allows for high-sensitivity room temperature sensing, at very low power consumption rates ($\mu$W to mW) per sensor. It is thought that these sensors have great potential for embodying a new generation of chemical sensors to detect chemical species. Carbon nanotube-based chemical sensors have the following properties:

- High sensitivity (potentially single-molecule/quantum-capture sensitivity) due to their extraordinarily high surface to volume ratio,
- Rapid detection rates due to their one-dimensional nanostructured sensing medium whose electronic properties are very sensitive to gas adsorption,
- Lower power consumption ($\mu$W to mW), which is ideal for persistent surveillance and environmental monitoring applications,

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- Small size and lightweight.

Our preliminary work with carbon nanotubes indicates a conductivity change with exposure to $NO_2$ at different concentrations and the detection limit of it is 44ppb (see figure 1), and to nitrotoulene (simulate of explosives) with a detection limit of 254ppb (see figure 2), as well as a variety of other organic and inorganic vapors and gases (see figure 3). Preliminary results also show sensitivity in the ppb range with reproducible sensitivity within 6% between sensors. By loading the carbon nanotubes with catalytic metal nano clusters and coating polymers on the surface of carbon nanotubes, excellent selectivity was achieved for room temperature detection of methane (combustible) in low ppm and chlorine (toxic) gas in ppb level.

Based on this nanosensor development described above, a 32-channel sensor array module loaded with different nanostructures has been developed for a space flight demonstration (see figure 4). This module will orbit the Earth at around 500kM and repeatedly demonstrate trace $NO_2$ detection.

Combining the carbon nanotube-based chemical sensor with MEMS technology, a lab-on-a-chip can be built, which has onboard data processing and potentially wireless communication capabilities. Such a lab-on-a-chip system can be deployed across a wide spectrum of hardware platforms for environmental monitoring, and can be made into a portable handheld device (see figure 5).
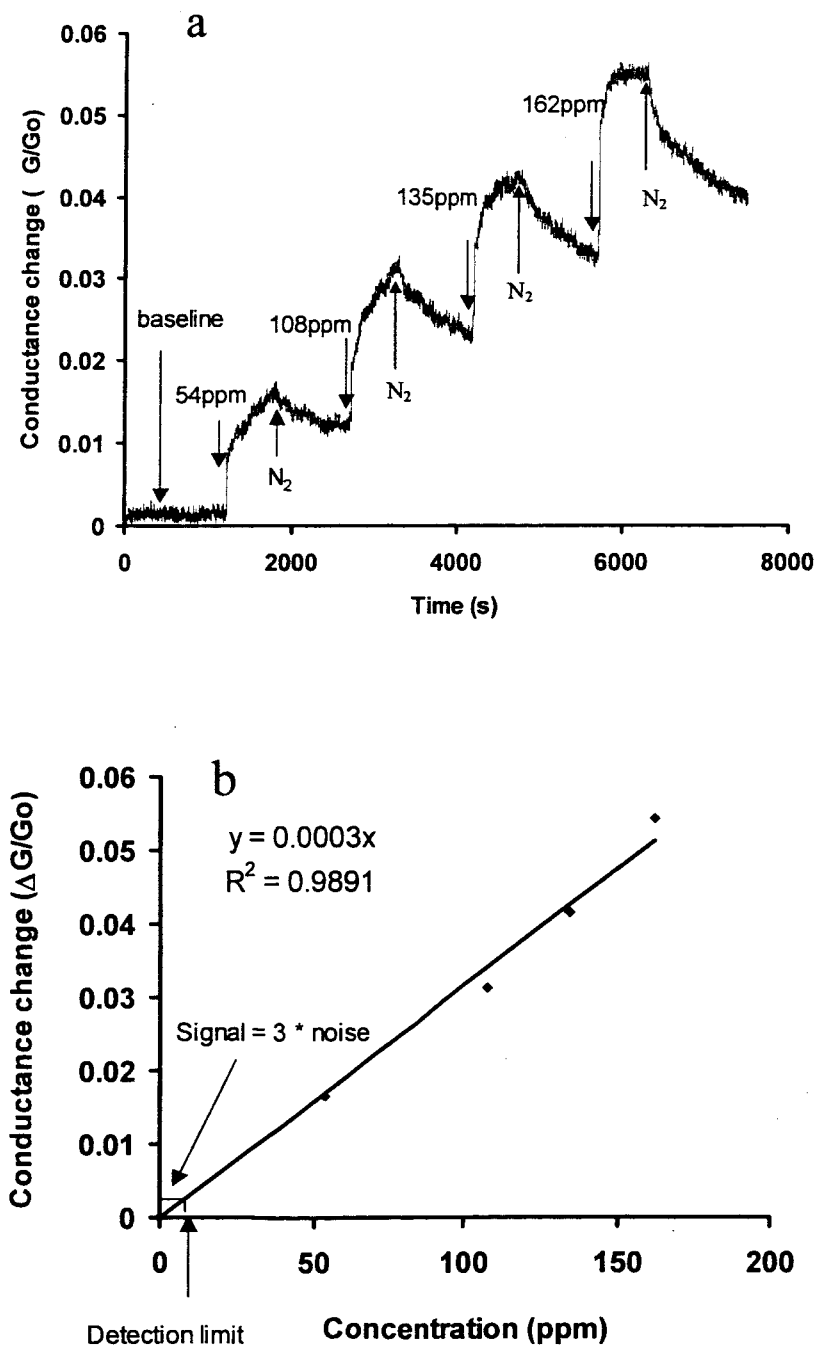
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*Figure 2: Representative sensor response from group 3 for nitrotoluene. (a) Sensor response is a step function of concentration; (b) Calibration curve from (a). The nitrotoluene vapor was evaporated using a bubbler with a 100 cc/min ultra pure nitrogen at room temperature and this vapor stream was further diluted by nitrogen to a total flow of 400 cc/min. The purge gas is nitrogen as well.*
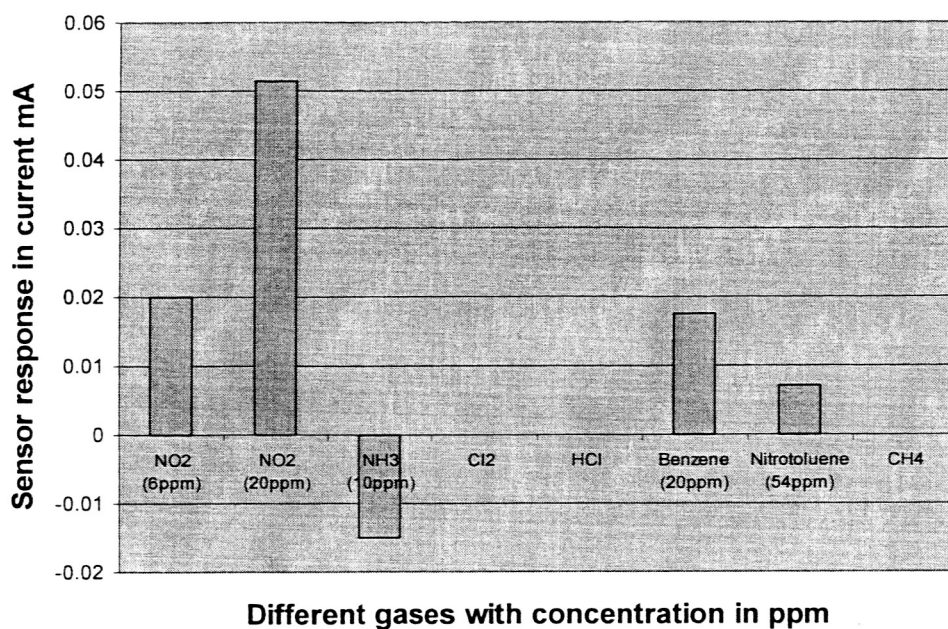
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*Figure 3a: Comparison of carbon nanotube sensors to different gases and vapors*



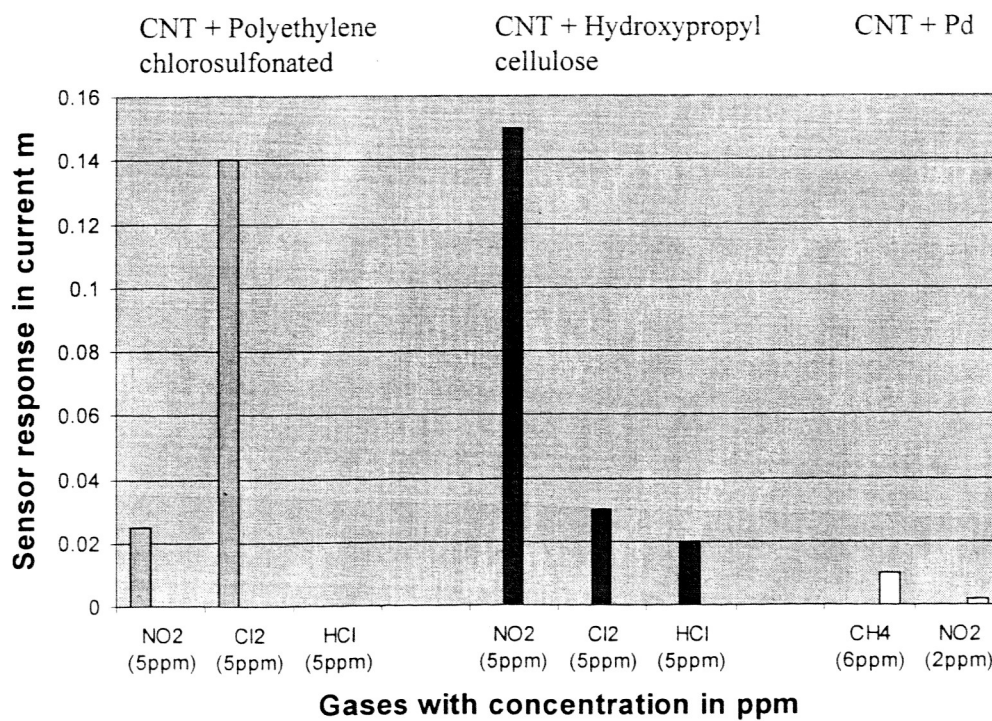*Figure 3b: Comparison of CARBON NANOTUBES with different mixing materials for gases*

# Flight Demo Unit for Satellite



Ceramic chip carrier

32-channel sensor chip
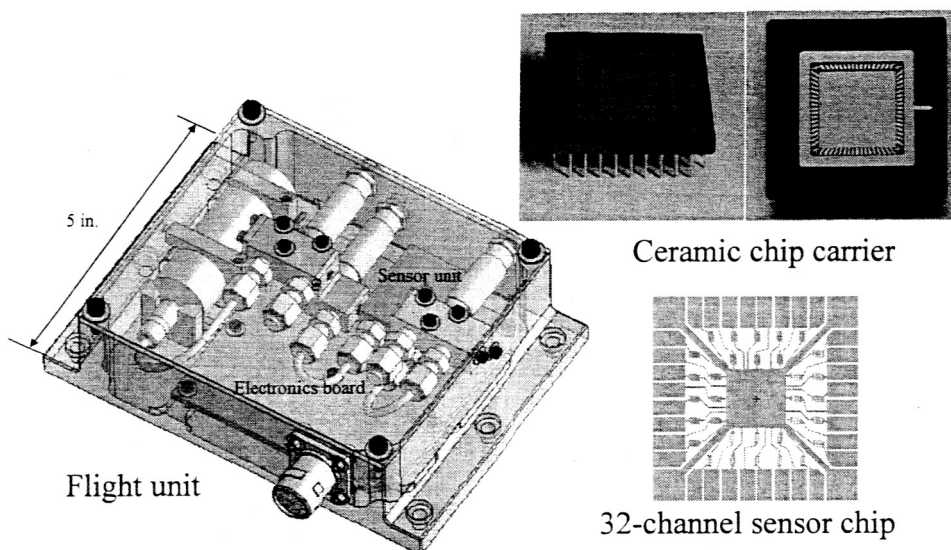
5 in.

Sensor unit

Electronics board

Flight unit

*Figure 4: A nanostructure-based multi-sensor module for a flight demonstration in space*
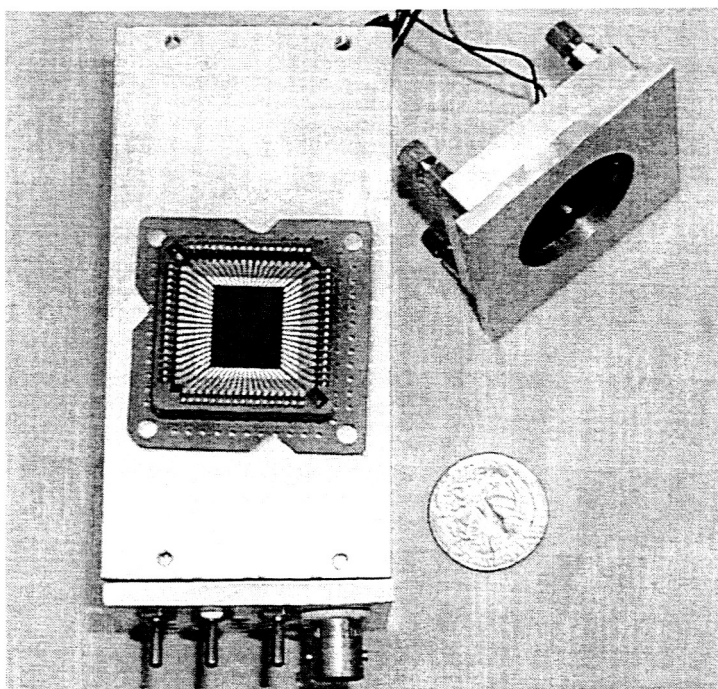


*Figure 5: A handheld device with a nanostructure-based chemical sensor array for in-situ chemical detection*

## 3. Baseline Use

In February 2002, the President Announced Clear Skies & Global Climate Change Initiatives (For Immediate Release, Office of the Press Secretary, February 14, 2002). One of the NASA mission is to understand and protect our home planet for which acquisition of data on "greenhouse" gases using uninhabited aircraft is required. These data validate satellite line-of-sight observations used to develop models for long-term, human-induced climate change. Currently, piloted aircraft are used and instrument volume, mass, and power needs are substantial. However, future Earth Science Enterprise (ESE) needs include airborne autonomous instruments with greatly reduced volume, mass, and power requirements. Research and development of Nanotechnology-based sensors and instruments can meet this need. It is believed that the emerging field of nanotechnology can play an important role in realizing these goals, and the proposed work represents a significant step in that direction. Within the Troposphere, the ESE priority species for study are $NO_2$ and CO. The need for nano sensors with dramatically reduced mass, volume, and power requirements is evident from ESE mission trends – away from large platform systems and toward longer-duration, more economical Uninhabited Arial Vehicles and high-altitude experiments. Future measurements in support of ESE will be focused upon answering questions related to:

1) The recovery of the stratospheric ozone layer,

2) Air quality and intercontinental transport of pollution, and,

3) Climate change that results from increases of human-produced greenhouse gases.

Also, in January 2004 the President Bush Announces New Vision for Space Exploration Program (For Immediate Release, Office of the Press Secretary, January 14, 2004) for NASA to extend and expand human presence in solar system to further our exploration and scientific goals. Smart chemical detection and environmental monitoring is one of the challenges that NASA is focusing on through the current effort on the human and robotic technology for space exploration. This requires the development of miniature detectors – which exhibit selectivity, sensitivity, and time response equal to or better than current state of the art sensor technology – that are compact, robust and have low mass & power budgets, requirements clearly satisfied by the sensor technology described in this document.

This proposed task will develop the miniature, chemical sensor systems which have multiple uses in power systems, propellant production, and planetary chemical analysis. A broad based, one-stop-sensor array meeting a broad range of needs is the objective of this sensor system. This group is leading in the development of micro, nano sensor technology for toxic gas and volatile organic vapors detection. The prototype chemical sensor developed for space flight demonstration has been progressively developed at NASA Ames and will be delivered to the U.S. Naval Academy in January 2005 for launch in 2006.

The product of our proposed work not only has potential use in interplanetary and space-based systems, but a wide spectrum of terrestrial civilian and defense applications. A sampling of terrestrial applications include: hydrogen sensors for fuel-cell applications; carbon monoxide and $NO_x$ sensors for emissions monitoring; ammonia and perfluoropropane in refrigerant leak monitoring; and carbon monoxide, ozone, and VOC sensors for air quality monitoring. As mentioned earlier that this technology was developed for explosives detection as well funded by

FAA. We have tested our nanosensors to nitrotoluene with a detection limit of 254ppb, chlorine gas in nitrogen (<2ppm), and hydrochloric acid in nitrogen (<5ppm). These chemicals are either a stimulant of explosives or toxic gases that are of interest to DOD or homeland security for early detection. We are currently working towards even lower detection limit of these substances in sub ppb concentration level. The high performance sensors developed here are also suitable for use in hostile environments and are amenable to miniaturization (both inherent benefits of solid-state sensors over most other gas sensor technologies). Competitive advantages for development of these technologies for the commercial market include fulfillment of several key market needs including increased sensitivity, higher reliability, and potentially fewer calibration cycles. Sensor users are constantly looking for technologies that offer low-cost and enhanced stability, lower detection limits and lower operating power, all improvements that the proposed technology should deliver.

Immediate uses of this sensor development also include the defense arena for hazardous gases and vapors detection. The Department of Defense has identified a requirement for 270,000 JCAD (Joint Chemical Agent Detector) systems. [More information is on the web at link: http://www.ids.na.baesystems.com/mads/products/jcad/jcad_1.htm]. The JCAD is a small, lightweight, high-performance chemical detection system that offers networked or stand-alone chemical detection. It can be hand-held or operated from a vehicle or from a fixed installation. Our sensing platform fits these specifications well and is well suited to excel in this application.

## Trends Impacting Improvement

There are several areas for potential improvement of this sensor technology for integration into future systems. They are:

1) Development of a broader array of Nanostructured sensing materials;

2) High-speed computing capability for signal acquisition and processing;

3) Nano printing and inkjetting technologies for enhanced fabrication process;

4) Wireless and distributed-network platform integration for broad-area applications.

*Nanostructured materials*: Nanostructured materials have unique structural properties, such as high surface area, single crystallinity, and well organized molecular structure. These properties are critical to chemical sensing due to the adsorption process prior to the chemical to electrical signal conversion. High surface area ensures high sensitivity, because the adsorption amount of chemical species is determined by partition coefficient. More molecules will adsorb onto the surface with the same concentration of chemical flow when the surface area is big. Therefore, bigger change in the material properties will be observed, which reflect a high sensitivity in sensor performance. Single crystallinity provides stability of the nanostructures for sensor operation at varies temperatures and a long duration. Metal oxides nano particles have been used in many types of sensors. Specific physiochemical properties, due to nanoscale, are utilized for better sensor performance in terms of sensitivity and fast response. However, the nanoparticles are not stable. They agglomerate to form bigger and bigger particles with the time and agglomerate fast at the elevated operating temperature. This is the biggest drawback for nano particle metal oxides sensors. The single crystal structure can maintain its size to offer long term stability and consistency of the sensor quality in batch quantity. The well organized molecular structure of nano materials can assure the repeatability and reproducibility of sensor performance by regular adsorption of

molecules in the nanostructures. Different types of nanostructured materials will be developed to make an orthogonal sensor array for sensitivity and selective chemical detection.

*High speed computing capability*: With the advance of the computing and computer technology, fast data acquisition and transformation of transient chemical signals is possible. This capability will provide a platform to advance the sensing technology from data collection and storage, signal processing, and information transformation point of view. Currently, an EEprom, with the size of 1 inch x 1 inch, has the process capability equivalent to a Pentium II to Pentium III. This device can be integrated onto a chip board for smart sensing. The collected chemical sensing signal can be pre-processed, post-processed, stored, and analyzed using pattern recognition techniques or neural network technique. Therefore, a miniaturized intelligent sensing system can be made. Fast data processing can also provide the capability for high density sensor array measurement.

*Nanoprinting and nanoinkjetting*: Currently, there are many efforts on nano printing and nano inkjetting technology to get more precise positioning of fluids loaded with various nanostructured materials at increasingly smaller drop diameters. Advancements in this area will impact our nanosensors for scale-up in mass production with automation capability and easy quality control process. The uniformity of the droplet will ensure the reproducibility from sensor to sensor. By varying the concentration of the nano materials suspensions and the droplet size, the initial state of chemical sensors can be targeted for optimal sensor performance.

*Wireless and network technology*: Taking advantage of wireless and distributed networking capability, our nanosensors can extend the market from existing point care or measurement to a network mapping measurement. For example, the nanosensors can be used for environmental monitoring and fire detection in each room and hallway in buildings. The wireless sensors can also be distributed in the battle field for monitoring the troop movement by detecting the smells of gasoline and sweater. These wireless sensors are spread like dust particles and they can transmit chemical signatures to the central station for warning.

## Alternative Approaches and Organizations

The challenges to advancing the development of this technology lie in enhancing the selectivity of the sensors and reducing the recovery time for sensor reuse. Alternative approaches can be taken to improve and ensure this technology development approach continues to lead the state-of-the-art. These alternative approaches can be grouped into to broad categories

1) Sensing materials,

2) Sensing platforms,

3) High density array.

*Sensing materials*: Semiconductor nanowires have been the subject of enthusiastic research efforts to enable a large variety of compositions, to incorporate dopants, and to investigate the promise of these structures to field-effect transistor, chemical and biological sensor, and optoelectronic technologies. Although many of these characteristics have been the subject of proof-

of-principle experiments, much work remains until semiconductor nanowires can be integrated into a commercially viable technology.

It is within the scope of this concept paper to suggest future integration of this alternative inorganic approach into the fully developed interdigitated electrode array.

***Sensing platforms***: In analogy to the bulk properties, unadulterated nanowires have been demonstrated to function as switches[7], diodes[7], and photonic nanodevices[8]. Related devices have been fabricated to demonstrate the sensitivity of these semiconductor nanostructures to chemical environment. Drawing on the principles of electrostatic gating, polar and charged analytes can be detected as a change in device conductivity[9, 10], sensitivity to atmospheric gases has been investigated[11] and various examples of biological sensing have been achieved[7, 12, 13].

The sensing platform, also called a transducer, can influence the sensor performance as well. A judicious coupling of sensing material with platform will enable high sensitivity and selectivity. Examples of alternative sensing mechanisms, employed in alternative configurations, include electrostatic gating of field effect transistors, thermopower of chemically sensitive thermisters, impedance change of capacitors, and barrier height modulation in Schottky diodes. It should be noted that the sensor array approach outlined in this concept paper can be hybridized with the above-mentioned platforms to optimize detection capability. Dan Powell and Stephanie Getty at NASA Goddard flight center have planed to and may have started to build up a nano device lab that can provide such devices for chemical sensing evaluation and for hybrid sensing system integration.

The complexity of the above-mentioned alternative technologies is highlighted by the intrinsic need for multi-level lithography. On average, devices fabricated to date within these alternative frameworks have relied on single, isolated components, and finding the location of these nanoscale components is time-and resource-consuming. The advantages of the IDE sensor platform over the more complex alternative platforms derive from the low complexity and built-in redundancy inherent to the IDE array.

***High density sensor array:*** Our nano sensor can be self-assembled to a high density ($10^3$-$10^6$/cm$^2$) array with low power consumption (at least 100 times less than the current analytical instrument used in space), light and compact (at least 10 times smaller than the current analytical instrument used in space), and with proved high sensitivity (ppb-ppt), accuracy and rapid response. High density sensor array can have a luxury to use redundant sensors for reducing the noise level by averaging the sensing signals from these replicates. Signal to noise ratio is crucial to extract useful information for accurate measurement. Inputs from high density nanosensor arrays will provide a high degree of discrimination that can accurately monitor and understand the local chemical environment and allow appropriate response on the part of the crew or vehicle system. It can also be used for homeland security and battlefield chemical weapon detection.

## 3. Leading Aerospace Applications

There are two broad categories of sensor application in aerospace. The first is to enable and enhance the autonomous science measurement capability for a given spacecraft, instrument, orbiter, or extraterrestrial rover. And the second is to enable and enhance realization of national and international goals for manned space exploration, resource extraction and utilization, and commerce.

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Within each of these broad areas, there is a subset of mission needs which are common to both and require compact, low mass and power chemical sensors. It is well established that two of the primary limiters to initiation of a space-based economy are the costs relating to getting mass to orbit (between $10,000/lb and $20,000/lb on average for NEO and an order of magnitude higher for Mars and other planets) and spacecraft health monitoring and safety. It is felt that the successful development and infusion of the robust, reliable, and long service-life chemical sensor, described above, into many if not all future aerospace missions would significantly reduce both system mass (via its compact size and low system density) and mission risk by generating a continual stream of vehicle health, environmental quality, and biohazard detection data to mission controllers, explorers, and astronauts. In addition to spacecraft and orbiting platform applications the sensor technologies described above are ideally suited for interplanetary applications.

Characterization and monitoring of alien environments are high priorities for both the exospheric science and exploration communities. The above sensor technologies when mounted on a planetary rover or aerorover or integrated into a distributed sensor network would be capable of providing precise, accurate, and continual environmental characterization data for a broad and increasing set of chemical species. Further, the sensors described above are sufficiently low mass and compact to be packaged in a portable, hand-held device for real-time composition measurements of spacecraft, extraterrestrial habitat, or alien environmental monitoring. The robust capability of these sensing technologies to accurately sense chemical species of interest in either liquid, gas, or on solidified matter only enhances their application potential.

Another application is to deploy nanosensors which ensure proper execution of processes in a microgravity or reduced gravity environment such as multiphase media, or systems strongly impacted by the lack of natural buoyancy, such as combustion and pre-combustion monitors. These and other unique microgravity considerations make some aspects of the current sensor technology development aerospace-specific but, as has been previously discussed, the performance of the current system on Earth still exceeds that of state-of-the-art in many respects. Microgravity transport modeling capability will be employed to enable interpretation of sensor data, such as localization of hazards. Sample acquisition for accurate monitoring must account for the complexities of multiphase (gas, liquid, solid) behavior in micro or reduced gravity, and must also require little or no crew time and expendables. Sample handling may be necessary to achieve the necessary sensitivity and selectivity. The recommended nanosensors can be used for External Environment Monitoring to monitor hazardous conditions in the extra-vehicular environment as well as interior to the science and exploration craft and habitats just described. Hazards in these regions include but are not limited to reactive chemicals, erosive dust, and radiation.

# 4.  Potential Non-Aerospace Applications

The current focus of development for the proposed technology has a specific application in space. However, as has been previously discussed, it has a wide spectrum of applications here on Earth including defense, industrial, environmental, medical, and biological applications.

*Industry:* Nanostructure based chemical sensors possess high sensitivity, small size and low power consumption, which can be used to quickly verify incoming raw materials at the delivery point; to monitor the changing composition of the vapor phase surrounding or contained within a given industrial process. Much like vision inspection is used to assess the visual integrity (color, shape, size) of products, olfactory inspection assesses the chemical integrity (consistency, presence of contaminants). These recommended chemical sensing technologies can significantly reduce the amount of time and money spent analyzing those materials in a lab, as well as reducing the amount of materials handling, while simultaneously removing the operations monitor from the environment and reducing overall process risk.

*Environment:* Increasing awareness and new regulations for safety and emission control make environmental monitoring one of the most desired amongst the numerous industrial and civil applications for which the development of reliable solid-state gas sensors is demanded. Current methods for air quality control approved by the standards consist of analytical techniques, which need the use of very costly and bulky equipment. For applications in this arena, sensors that are able to selectively detect various gases at a concentration level of a few ppb and in the form of low-cost portable handheld devices for continuous in-situ monitoring are needed. With unique advantages of high sensitivity, small size and low power consumption, and strong mechanical and thermal stability, carbon nanotube based chemical sensors are best fit for this type of application.

*Defense:* Chemical sensors are very focused for security and defense applications due to their portability and low power consumption. Carbon nanotube sensors potentially can offer higher sensitivity and lower power consumption than the state-of-the-art systems, which make them more attractive for defense applications. Some examples include monitoring filter breakthrough, personnel badge detectors, embedded suit hermiticity sensors and other applications. Additionally, a wireless capability with the sensor chip can be used for networked mobile and fixed-site detection and warning systems for military bases, facilities and battlefield areas.

*Medical/Bio:* It is believed that chemical sensors would provide physicians with a quicker and more accurate diagnostic tool. Applications could include obtaining objective information on the identity of certain chemical compounds in exhaled air and excreted urine or body fluids related to specific metabolic conditions, certain skin diseases or bacterial infections, such as those common to leg or burn wounds. Additionally, the chemical sensors may provide more accurate, real-time patient monitoring during anesthesia administration.

It is noteworthy that the sensing platform developed in this project can also be used in liquid phase for heavy metals and pH detection, as well as for bio species detection, such as pathogen, bacteria, and enzymes. It can be also used for headspace sample analysis and detection of solid substances.

## 5.  Drivers for Change

Chemical sensors currently on the market have already demonstrated the necessity of nano materials with high surface area for analyte capture. Surface roughening is employed in various approaches to enhance surface area, one consequence of which is the associated compromise of electronic properties upon the introduction of disorder. The preservation of crystalline order that coexists with the inherent surface area enhancement of organic and inorganic nanowires illustrates one of their major advantages.

The high operating temperatures requisite to conventional metal oxide gas sensors also suggest an area of improvement. In fact, our preliminary investigations into nanostructured metal oxide sensors (ZnO) suggest that operating temperatures are significantly reduced upon reduction to the nanoscale. The cylindrical configuration of these prototypical devices indicates that surface energy is an important parameter in operating temperature considerations.

Surface energy is intimately tied to surface structure, and further techniques to modify surface structure can be investigated through the concept of functionalization that can also improve the selectivity, sensitivity, and response time.

## 6.  Recommended Approach(es)

The scope of possibilities that is demonstrated by these early devices suggests a significant payoff for future development. Our extensive knowledge of the surface chemistry of nanostructures combined with a simple sensing platform, IDE, suggests the potential for a large assortment of near-term applications. Specific objectives and milestones are as follows:

1.  Improve sensor sensitivity and response time;

2.  Investigate materials and techniques appropriate to enhance sensor selectivity and stability;

3.  Study environmental effects, such as humidity, temperature and altitude/pressure, for sensor rooftop test and aircraft flight tests;

4.  Optimize sensor design and the electrode/transducer platform process;

5.  Design a data acquisition system;

6.  Investigate the impact of data processing protocols to the precision and accuracy of chemical detection;

7.  Demonstrate a proper handheld device for in-situ chemical detection.

A9 Nano Sensors and Devices

**Approaches:**

### 1. Sensitivity and response time

The proposed sensing platform is a resistive chemical sensor based on an observed change in nanostructured device conductivity when a chemical species adsorbs to the nanostructures. Chemical adsorption is key to generating a sensor signal through conversion of chemical capture to electrical impulse. Chemical adsorption depends on several structural (i.e., the surface area, pore size, and pore distribution) and electrical (i.e., charge donor or acceptor) properties, which determine sensor sensitivity and response time. As described in referenced materials [4], SWNTs can be thought of as a rolled-up graphene sheet (figure 6). Each carbon atom is on the surface of the tube and therefore sensitive to the environment it is exposed to, both chemical and electrical. A
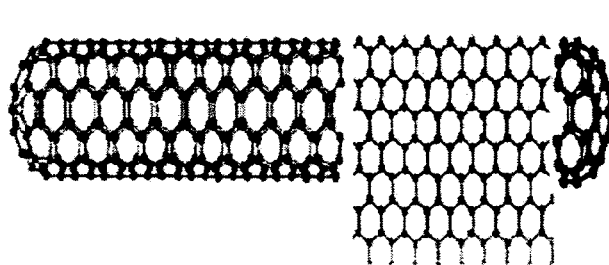


*Figure 6:. Schematic of a single walled carbon nanotube. Note the closed ends (half fullerene molecules) which maybe opened by oxidation.*

small change in the charge environment will cause a large change in electrical current at room temperature. We studied the structure of single-walled carbon nanotubes [11], and through an in-house two-step purification process we have obtained clean SWNTs with a surface area of ~1587 $m^2/g$. Such a large surface area provides a huge bed for molecular adsorption. Each molecular adsorption will cause a change of the electronic conductivity of the SWNT device resulting in an electrical signal. In principle, the sensor response time should be very fast due to the large, easily accessible surface area. However, SWNTs are typically packed together as rope-like bundles reducing the net exposed adsorption area. One opportunity for improving the response time as well as sensitivity of the proposed sensor is de-bundling the individual nanotubes. We anticipate that we can optimize the selection of solvent used for SWNT dispersion to achieve enhanced SWNT separation as well as optimal pore size and distribution within SWNT matrix.

Similarly, the sensor response time is also a function of surface area that influences the molecular adsorption. The larger the exposed surface area, the faster the response. However, increased adsorption surface areas will tend to lengthen sensor recovery time. In our preliminary study using $NO_2$, a UV lamp was used to illuminate the sensor after exposure to shorten recovery time. Using the UV lamp, recovery time was reduced from more than 10 hours to less than 15 minutes. The 254 nm UV light provided energy, which decreased the surface energy of the SWNTs, resulting in the release of $NO_2$ and the recovery to the SWNTs base state. A lightweight UV diode can easily be incorporated into the sensor chip for real gas monitoring. Other possibilities for reducing recovery time exist, including heating of the sensing element. In the event this approach

is not successful, we can easily configure tens of SWNT sensors in a configuration like that to be shown below in figure 8 wherein sensors are exposed to the gas sample and recording signals while others are in the process of recovery. The end result is a detector that can meet the requirement to sample chemical species at two-minute intervals. Another technique to alter the response time is to use a sensor array by turning on each channel individually and let the rest of the channels recover. In this case, if we use 10 channels, the response time can be reduced 10 times. So, the high density sensor array can be very powerful in this measurement design and configuration to speed up the response time.

### 2. Selectivity and Stability

Selectivity is a universal issue for current conventional sensors, and it is correlated to the sensor's sensitivity. Normally, if the sensor is very sensitive it can be sensitive to many chemical species. In order to improve the selectivity, many times the sensitivity is sacrificed to make it sensitive to only one chemical species with less sensitivity and lose the sensitivity to others. This balance resulting sensitivity is not high enough for the conventional sensor in some applications. SWNTs devices have a certain degree of selectivity, as they are sensitive to different types of molecules in different way. However, this level of selectivity is very limited in real world applications.

We have three possibilities for improving selectivity:

1) Modify the surface of nanostructures, such as carbon nanotubes or metal oxides nanowires and nanobelts with functional groups, such as a carboxylic end-group for sensing basic molecules, an amine end-group for sensing acidic molecules, and aromatic end-groups for sensing large organic molecules, based on the principle of "like dissolves like."
2) Dope the nanostructured materials (e.g. carbon nanotubes) with catalytic metal clusters, such as Pd for hydrogen, Pt and Ag for hydrocarbon, and Cu and Rh for nitric compounds. In this case, the carbon nanotube will act as a matrix that holds the metal binding sites for chemical sensing.
3) Coat the surface of carbon nanotubes and other conducting nanostructures with different polymers – such as polystyrene, polyvinyl alcohol, etc. used in commercial polymer based chemical sensing arrays for organic vapor detection – that   provide specific interactions with the chemical species of interest. Some of the surface area may be lost by these chemical treatments, hence reduced sensitivity. However, as this chemical treatment aims to get a specific interaction between the carbon nanotube matrix and gas molecules, it should improve the selectivity while maintaining the high SWNT sensor sensitivity.

SWNTs are mechanically very strong and can sustain temperatures up to 400°C. These properties ensure that the carbon nanotubes are a stable sensing material. We also took into account the stability in the proposed sensor design and assembly in a preliminary study [nanoletters]. The investigators designed a pair of interdigitated electrodes with long strip of electrode area. The network type of carbon nanotubes formed across two electrodes comprises of thousands of carbon nanotubes. If one nanotube does not give a good contact, the others will. Statistically, the matrix of carbon nanotubes not only possesses a good contact with gold electrodes, but also maintains a stable platform for chemical sensing. Other nanostructures should have similar properties as carbon nanotubes.

### 3. *Environmental Effects: Humidity, Temperature and Altitude/Pressure*

There is no reported study of the environmental effects of carbon nanotube based sensors. This is an important factor that must be explored since the sensor is designed for use in the earth's atmosphere. We plan to study the relationship between sensor responses and the humidity and temperature in an environmental chamber; a handheld testing device needs to be used for the altitude test at various levels.

We propose two approaches for the sensor in the real application, if there is any environmental effect:

1) Establish a mathematic model for these effects for the purposes of creating a self-correction event during the measurement.
2) Determine a reference sensor with which to make a differential measurement.

The results of environmental effects will guide the operation of the sensor for rooftop and flight tests.

### 4. *Design and Process of the Nanosensors*

We have designed and fabricated a single pair of IDEs in a preliminary development of an $NO_2$ detector. The team at NASA Ames has also designed and fabricated a chip with an array of 12 sensing elements (12 IDEs, see figure 7) and 32 sensing elements (32IDEs, see Figure 8), which can accommodate different combinations of sensing materials for chemical detection simultaneously in a complex background. The proposers plan to add heaters underneath the IDEs, so that the sensors can be operated at a controlled temperature to improve the sensor's stability.
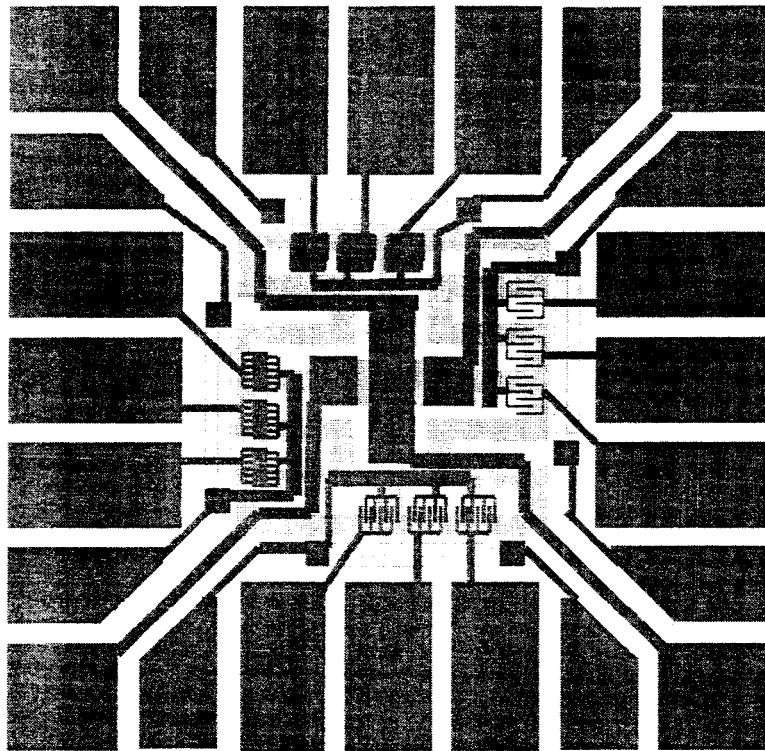
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*Figure 7: Twelve sensing elements on a chip (1cm x 1cm) with heaters and thermistors.*
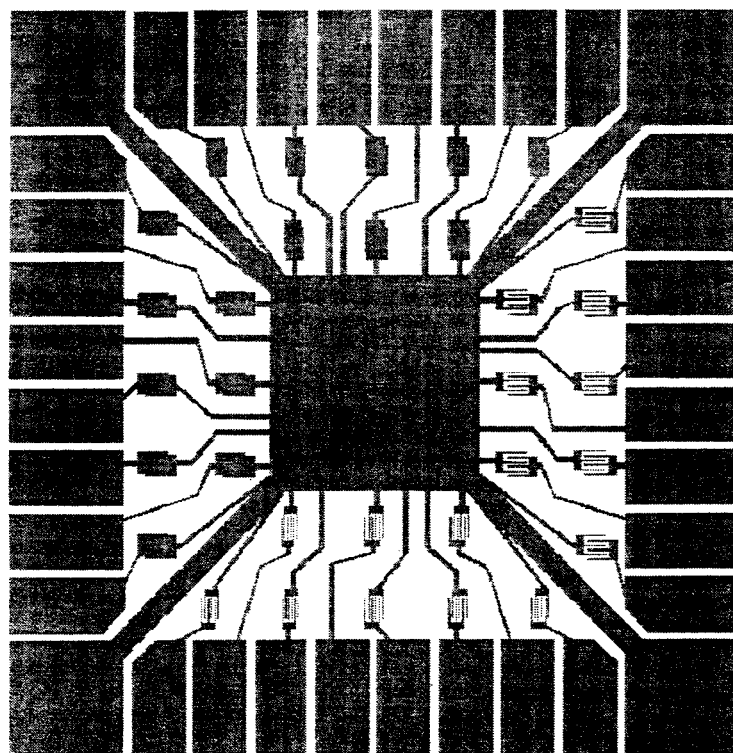
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*Figure 8: Thirty two sensing elements on a chip (1cm x 1cm) for array sensing.*

The material process for making a sensor directly affects the sensor performance through the final morphology of the sensing layer. There are two ways of depositing the carbon nanotubes onto the IDE:

1). Solution Casting: Carbon nanotubes are dispersed in a solvent, providing a uniform and stable suspension. The solution is then pipetted onto the IDE. After the solvent evaporates, the carbon nanotubes are attached to the IDE by a static charge bond between C-Au/Pt. This is the approach used in our preliminary work on the $NO_2$ detector.

2). In-situ growth of carbon nanotubes: In catalyst-assisted chemical vapor deposition (CVD), the IDE area is patterned with a coating of a thin catalytic layer, usually Fe/Al for single-walled carbon nanotubes and Ni for multi-walled carbon nanotubes. The carbon nanotubes will grow only from the catalyst patterned on the IDE area. The contact between the metal fingers of IDE and the carbon nanotube is through a C-Ni or Fe/Al- Pt chemical bond. In this case, the metal for the IDE is platinum, not gold, since gold inhibits carbon nanotube growth.

When the modification of carbon nanotubes is needed, it can be done prior to the carbon nanotube deposition or after. The modification can be done chemically or electrochemically.

### 5. Design a Data acquisition system

Detector electronics will consist of power supplies, ammeters, preamplifiers, and temperature and UV generator controls. Particular attention will be paid to reduction of low frequency noise e (1/f), small size and low power.

The interface will allow transfer of the conditioned signal (pre-amplified or A/D converted) to the computing unit.

The computing unit will allow data acquisition, processing and storage, and when appropriate, offer a user interface.

### 6. Impact of Data Processing Protocols

Data processing is critical in chemical sensing for obtaining accurate and precise information. It is also application-dependent.

Electronic measurements are always accompanied by high frequency noise. Because a high signal to noise ratio (SNR) is crucial for extracting chemical information, especially when the concentration of sample is low, it is important to boost the signal relative to the noise using digital filtering techniques. These techniques also can help to improve the repeatability between exposures. The Savitsky-Golay filter is used to smooth the response curve using a polynomial fit. The filter window can be adjusted in terms of number of data points, which give the best smoothing without significant distortion.

If a sensor array approach is used, post-processing with different data scaling techniques and pattern recognition techniques will be explored for this type of sensor and application. For example, principal component analysis (PCA) can be used for the outlier diagnosis. And four other supervised algorithms can be used for building a model and predicting the unknowns: K-nearest neighbor (KNN), Soft Independent Modeling of Class Analogy (SIMCA), Fisher Linear Discrimination (FLD), and Canonical Discriminant Analysis (CDA).

### 7. Demonstrate a proper handheld device for in-situ chemical detection

The detector/sensor prototypes will be designed to allow handheld use and operation from batteries, with a user interface provided by an external portable computer or PDA. The development of detector prototypes for rooftop tests and flight tests will be divided in 4 engineering subtasks illustrated in figure 9 and detailed below.

Figure 9: Structure of the detector:
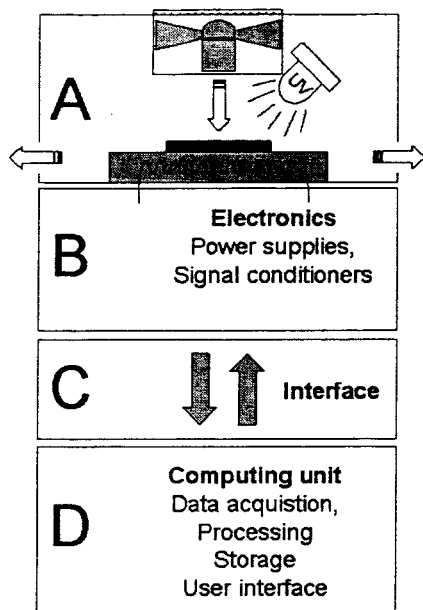
A: sensor conditioning unit with sample collection and delivery, sensor temperature control and UV generation for sensor regeneration. A specific conditioning unit will be designed for each testing condition (rooftop, and airborne tests)

B: detector electronics unit including power supplies for sensor and controls, ammeter and signal conditioners. Emphasize on low noise (1/f), small size and low power.

C: Interface unit for sensor data and control I/O. Analog interface for year 1, digital interface (USB or RS232) from year 2.

D: Computing unit. PC with analog I/O card and Labview program for year 1. PC with digital I/O and Labview program for year 2. Imbedded processing unit for year 3.

**A**

**B** Electronics
Power supplies,
Signal conditioners

**C** Interface

**D** Computing unit
Data acquistion,
Processing
Storage
User interface

# 7. Rationale for Technical Approach

The above-recommended approaches are commonly used in commercial sensor technologies. Our design of the sensing platform using the IDE design is mature and easy to work with. Because the sensing material is the key to chemical sensing, the availability of an agile platform that is compatible with nanoscale materials gives us unprecedented access to new and varied sensing elements. Nanostructured materials are an attractive class of materials to explore because they provide not only the unique physiochemical properties in nanoscale, but also a well organized atomic-scale structure for us to investigate the effects of quantum confinement and the tunability of energy scales. This gives us a substantial opportunity in creativity to enhance the sensor performance through the modification and stimulation of nanostructured materials.

The technical team has variety knowledge background in chemistry, physics, materials science, analytical instrumentation and nanotechnology.

# 8. Summary of Prototype Identification and potential Implementation Plan

The practical objectives of this development are:

- Design and fabricate nanostructure engineered chemical sensor array with 32 channels. (year 1-2)
- Design, fabrication and tests of a static system for Lab test (year 1).
- Testing of an evolved static system at a range of atmospheric pressures in a chamber readily available for field test. (year 1-2)
- Design and fabrication of a prototype of sensor array chip for multi purpose use. (year 2)
- Design and fabricate a prototype of a handheld device for demonstration in field test. (year 3)

Specific objectives and milestones are as follows:

- Improve sensor sensitivity and response time to gases and vapors (e.g. $NO_x$, toluene, etc),
- Investigate materials and techniques appropriate to enhance sensor selectivity and stability
- Study environmental effects, such as humidity, temperature and altitude/pressure, for sensor performance
- Optimize sensor design and the electrode/transducer platform process
- Investigate the impact of data processing protocols to the precision and accuracy of chemical detection
- Demonstrate a proper handheld device for in-situ chemical detection

# 9. Potential Investment Possibilities and Risk

This nanosensor technology is ready for mass production in commercial market. The prototype of the nanosensors can be easily derived from the sensor module that is currently under development for a flight demonstration experiment and that will be delivered to the satellite carrier by end of February 2005.

With the technology readiness and a wide spectrum of applications, potential investment possibilities can be from venture capitals, industry partners, and government contracts.

Risk: 1) intellectual properties management; 2) infrastructure for scale up production; 3) resources assurance.

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